



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C11D 1/825, 3/37, 17/00, 3/06, 3/02, 3/36</p>	<p>A1</p>	<p>(11) International Publication Number: WO 98/30662</p> <p>(43) International Publication Date: 16 July 1998 (16.07.98)</p>
<p>(21) International Application Number: PCT/US98/00452</p> <p>(22) International Filing Date: 6 January 1998 (06.01.98)</p> <p>(30) Priority Data: 08/782,336 13 January 1997 (13.01.97) US</p> <p>(71) Applicant: ECOLAB INC. [US/US]; Ecolab Center, St. Paul, MN 55102 (US).</p> <p>(72) Inventors: LENTSCH, Steven, E.; 21 Orme Court, St. Paul, MN 55116 (US). MAN, Victor, F.; 1410 Carling Drive #207, St. Paul, MN 55108 (US). IHNS, Deborah, A.; 1279 Jefferson Avenue, St. Paul, MN 55105 (US). MAIER, Helmut, K.; 115 Florida Court, Golden Valley, MN 55426 (US). SCHULZ, Rhonda, K.; 833 Ivy Lane, Eagan, MN 55123 (US).</p> <p>(74) Agent: DAIGNAULT, Ronald, A.; Merchant, Gould, Smith, Edell, Welter & Schmidt, P.A., 1000 Norwest Center, 55 E. Fifth Street, St. Paul, MN 55101 (US).</p>		<p>(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published</p> <p><i>With international search report.</i></p> <p><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: A COMBINATION OF A NONIONIC SILICONE SURFACTANT AND A NONIONIC SURFACTANT IN A SOLID BLOCK DETERGENT</p>		
<p>(57) Abstract</p> <p>The invention relates to a highly alkaline or mildly alkaline detergent composition having enhanced cleaning properties. The detergent combines a source of alkalinity and a blend of nonionic alkoxyated surfactant and nonionic alkoxyated silicone surfactant that enhances cleaning waxy-fatty soils. The composition may be in the form of solid block.</p> <div data-bbox="649 1176 1364 1806"> </div>		

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A COMBINATION OF A NONIONIC SILICONE SURFACTANT AND
A NONIONIC SURFACTANT IN A SOLID BLOCK DETERGENT

FIELD OF THE INVENTION

5 The invention relates to a laundry, warewashing, CIP, hard surface, etc. detergent composition that can take the form of a powder, pellet, brick or solid block detergent. Each physical embodiment of the detergent can be packaged in an appropriate packaging system for
10 distribution and sale. Typically, the detergent composition contains a source of alkalinity and an improved surfactant package that substantially improves soil removal and particularly improves soil removal of waxy/fatty soils common in a number of soil locations.

15 The invention also relates to an alkaline warewashing detergent composition in the form of a flake, powder, pellet, block, etc., using a blend of surfactants to enhance cleaning properties. More specifically, the invention relates to an alkaline
20 cleaning system that contains a source of alkalinity, a cooperating blend of surfactants and other cleaning materials that can substantially increase the cleaning capacity, relating to specific fatty or waxy soils. The detergent can also contain a variety of other chemical
25 agents including water softening agents, sanitizers, sequestrants, anti-redeposition agents, defoaming agents, etc. useful in detergent compositions useful in many applications.

30 BACKGROUND OF THE INVENTION

Detergent compositions comprising a source of alkalinity, a surfactant or surfactant package combined

with other general washing chemicals have been known for many years. Such materials have been used in laundry products, warewashing compositions, CIP cleaners, hard surface cleaners etc. Virtually any cleaner containing
5 a source of alkalinity that is designed or formulated for dilution into an aqueous based composition can be used within this broad general concept. The powder dishwasher detergents are disclosed in, for example, in Dos et al., U.S. Patent No. 3,956,199, Dos et al., U.S.
10 Patent No. 3,963,635. Further, Macmullen et al., U.S. Patent No. 3,032,578 teach alkaline dishwashing detergents containing a chlorine source, an organic phosphonate, a surfactant composition and a water treating agent. Similarly, Almsted et al., U.S. Patent
15 No. 3,351,557, Davis et al, U.S. Patent No. 3,341,459, Zimmerman et al., U.S. Patent Nos. 3,202,714 and 3,281,368 teach built liquid laundry detergent comprising a source of alkalinity and nonionic surfactant materials.

20 Powdered general purpose, warewashing and laundry detergents have been used for many years. The manufacture and use of solid block cleaning compositions were pioneered in technology disclosed in Fernholz et al., U.S. Reissue Patent Nos. 32,763 and 32,818 and in
25 Heile et al., U.S. Patent Nos. 4,595,520 and 4,680,134. Gansser, U.S. Patent No. 4,753,441, presents a solid detergent technology in a cast solid form using a nitrilotriacetate sequestrant. The solid block detergents move quickly replaced a large proportion of
30 conventional powder and liquid forms of warewashing detergents and other products in commercial, institutional and industrial laundry, warewashing etc.

washing and cleaning markets for safety convenience and other reasons. The development of these solid block cleaning compositions revolutionized the manner in which many cleaning and sanitizing compositions including
5 warewashing detergent compositions are manufactured and used in commercial, institutional and industrial cleaning locations. Solid block compositions offer certain advantages over conventional liquids, powders, granules, pastes, pellets and other forms of detergents.
10 Such advantages include safety, improved economy, improved handling, etc.

In the manufacture of powdered detergents, powdered ingredients are typically dry blended or agglomerated in known manufacturing facilities to produce a physically
15 and segregation stable powder composition that can be packaged, distributed and sold without substantial changes in product uniformity. Liquid materials are commonly blended in aqueous or nonaqueous solvent materials, diluted with a proportion of water to produce
20 an aqueous based liquid concentrate which is then packaged, distributed and sold. Solid block detergent compositions are commonly manufactured and formed into a solid often using a hardening mechanism.

In the manufacture of solid detergents, various
25 hardening mechanisms have been used in the manufacture of cleaning and sanitizing compositions for the manufacture of the solid block. Active ingredients have been combined with a hardening agent under conditions that convert the hardening agent from a liquid to a
30 solid rendering the solid material into a mechanically stable block format. One type of such hardening systems is a molten process disclosed in the Fernholz patents.

In the Fernholz patents, a sodium hydroxide hydrate, having a melting point of about 55°-60°C, acts as a hardening agent. In the manufacturing process, a molten sodium hydroxide hydrate liquid melt is formed into
5 which is introduced solid particulate materials. A suspension or solution of the solid particulate materials in the molten caustic is formed and is introduced into plastic bottles called capsules, also called container shaped molds for solidification. The
10 material cools, solidifies and is ready for use. The suspended or solubilized materials are evenly dispersed throughout the solid and are dispensed with the caustic cleaner.

Similarly, in Heile et al., an anhydrous carbonate
15 or an anhydrous sulfate salt is hydrated in the process forming a hydrate, having a melting point about 55°C, that comprises proportions of monohydrate, heptahydrate and decahydrate solid. The carbonate hydrate is used similarly to the caustic hydrate of Fernholz et al to
20 make a solid block multicomponent detergent. Other examples of such molten processes include Morganson, U.S. Patent No. 4,861,518 which discloses a solid cleaning concentrate formed by heating an ionic and nonionic surfactant system with the hardening agent such
25 as polyethylene glycol, at temperatures that range greater than about 38°C to form a melt. Such a melt is combined with other ingredients to form a homogeneous dispersion which is then poured into a mold to harden. Morganson et al, U.S. Pat. No. 5,080,819 teaches a
30 highly alkaline cast solid composition adapted for use at low temperature warewashing temperatures using effective cleaning amounts of a nonionic surfactant to

enhance soil removal. Gladfelter, U.S. Patent No. 5,316,688 teaches a solid block alkaline detergent composition wrapped in a water soluble or water dispersible film packaging.

5 Solid pelletized materials are shown in Gladfelter, U.S. Patent Nos. 5,078,301, 5,198,198 and 5,234,615 and in Gansser U.S. Pat. Nos. 4,823,441 and 4,931,202. Such pelletized materials are typically made by extruding a molten liquid or by compressing a powder into a tablet
10 or pellet. Extruded nonmolten alkaline detergent materials are disclosed in Gladfelter et al., U.S. Patent No. 5,316,688.

These powdered, pellet, liquid and solid block detergent compositions have acceptable cleaning
15 properties for most commercial purposes. Materials introduced into customer based testing or sold in the market place have achieved commercially acceptable and uniformly passing cleaning results. However, we have found, under certain conditions of fabric, ware,
20 substrate, water hardness, machine type, soil type and load, etc., some stains have resisted removal during the cleaning process. We have found a number of waxy-fatty soils that appear to harden on the surface of ware and resist even highly alkaline cleaning detergents under
25 certain conditions. Such soils are common in the cleaning environment and are typically hydrophobic materials that can form thin films on the surface of a variety of items. We have found that lipsticks soils can act as a soil model for this broad hydrophobic waxy-
30 fatty soil genus. Lipsticks typically contain a large proportion of lipid, fatty and wax-like materials in a relatively complex mixture including waxy compositions,

fatty materials, inorganic components, pigments, etc. The wax-like materials typically include waxes such as candelilla wax, paraffin wax, carnuba wax, etc. Fatty ingredients typically include lanolin derivatives,

5 isopropyl isostearate, octyl hydroxy stearate, castor oil, cetyl alcohol, cetyl lactate, and other materials. Such lipid materials are typically difficult to remove under the best of circumstances. More importantly, we believe the castor oil component of lipstick

10 formulations are unsaturated materials that can act like drying oils and can oxidatively crosslink in thin films to form crosslinked or pseudocrosslinked soil layers that are highly resistant to detergents. The formation of lipstick soils and other similar thin film, fatty or

15 waxy, soils resistant to removal has been a stubborn soil requiring attention for many years. Under certain circumstances such waxy-fatty soils can remain on glassware, cups, flatware, dishware, etc.

A substantial need exists to improve the cleaning

20 properties of solid block detergent materials and particularly as it relates to hydrophobic (fatty, crosslinked fatty or waxy) soils for which lipstick stains are a good model.

A number of avenues can and have been explored in

25 such an improvement attempt. Examples of research areas can include experimentation in the effects of water temperature, sequestrants that reduce water hardness, the effect of various alkaline sources, the effects of sequestrant types and blends, solvents effects and

30 surfactant choice. The surfactants that can be used in the cast solid materials are vast. There are large numbers of anionic, nonionic, cationic, amphoteric or

zwitterionic, etc. surfactants that can be used singly or in combinations of similar or diverse types. Even after substantial experimentation, waxy-fatty soils continue to pose a serious problem.

5

BRIEF DESCRIPTION OF THE INVENTION

The invention relates to a detergent composition having a blend of surfactants that substantially enhance cleaning properties of a detergent composition for
10 removal of stubborn hydrophobic soils including waxy-fatty soils for which lipstick stains are a good soil model. The detergent compositions of the invention can be formulated in a variety of product formats including liquid, powder, pellet, solid block, agglomerate powder
15 etc. The detergent composition comprises a source of alkalinity with a first nonionic surfactant and a second nonionic substituted silicone surfactant. The combination of a first nonionic surfactant and a second nonionic silicone surfactant, produces surprisingly
20 effective removal of hydrophobic waxy-fatty soil from the surface of ware. The second nonionic silicone surfactant and the nonionic surfactant cooperate to reduce surface tension to a surprising degree. The surface tension reduction appears to be roughly related
25 to soil removal. The combination of surfactants also appears to affect the interface between the soil and the ceramic or siliceous surface of glassware or tableware.

For the purpose of this patent application, the term "nonionic surfactant" typically indicates a
30 surfactant having a hydrophobic group and at least one hydrophilic group comprising a $(EO)_x$ group wherein x is a number that can range from about 1 to about 100. The

combination of a generic hydrophobic group and such a hydrophilic group provides substantial surfactancy to such a composition. The nonionic silicone surfactant is typically a surfactant having a hydrophobic silicone (polydimethyl siloxane) group with at least one pendent hydrophilic group or groups that can comprise $(EO)_x$ wherein x is a number of about 1 to about 100 in a surfactant molecule. The first nonionic surfactant can comprise any nonionic surfactant such as a silicone free nonionic surfactant or a nonionic silicone surfactant, however, the second nonionic substituted silicone surfactant cannot comprise a nonionic free of a hydrophobic silicone group.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a drawing of a current embodiment of the solid block detergent of the invention. The solid block having a mass of about 3.0 kilograms is made in an extrusion process in which individual or selected mixed components are introduced serially through material introduction ports into an extruder, the extruded block is formed with a useful profile at the extruder exit die and is divided into useful 3.0 kg blocks after extrusion. Once hardened, the material can be packaged (e.g.) in a shrink wrap that can be removed before use or dissolved during use.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The detergent composition of the invention combines a source of alkalinity, a first nonionic surfactant and a second nonionic silicone surfactant in an alkaline

detergent composition. Optionally, the compositions of the invention can also include a solidifying agent, sequestrants, sanitizing and disinfectant agents, additional surfactants and any variety of other
5 formulatory and application adjuvants. The term detergent composition should be interpreted broadly to include any cleaning, soil conditioning, antimicrobial, soil preparatory, etc. chemical or other liquid, powder, solid, etc. composition which has an alkaline pH and the
10 surfactant blend of the invention in the different physical formats discussed above.

 The first nonionic surfactants useful in the present invention may be solid or liquid. The nonionic surfactant is used in the compositions of the present
15 invention in an amount from about 0.5% to about 50% by weight, preferably from about 1.0% to about 40% by weight, and most preferably from about 2.0% to about 30% by weight.

 Most commonly, nonionic surfactants are compounds
20 produced by the condensation of an ethylene oxide (forming groups that are hydrophilic in nature) with an organic hydrophobic compound which can be aliphatic, alkyl or alkyl aromatic (hydrophobic) in nature. The length of the hydrophilic polyoxyethylene moiety which
25 can be condensed with another particular hydrophobic compound can be readily adjusted, in size or combined with (PO) propylene oxide, other alkylene oxides or other substituents such as benzyl caps to yield a water-soluble compound having the desired degree of balance
30 between hydrophilic and hydrophobic elements.

 Examples of suitable types of nonionic surfactant include the polyethylene oxide condensates of alkyl

phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide. Ethylene oxide being present in amounts equal to 5 to 20 moles of ethylene oxide per mole of alkyl phenol. Examples of compounds of this type include nonyl phenol condensed with an average of about 9.5 moles of ethylene oxide per mole of nonyl phenol, dodecyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol, dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol, diisooctylphenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-610 marketed by the GAF Corporation; and Triton CF-12, X-45, X-114, X-100 and X-102, all marketed by the Rohm and Haas Company.

The condensation products of aliphatic alcohols with ethylene oxide can also exhibit useful surfactant properties. The alkyl chain of the aliphatic alcohol may either be straight or branched and generally contains from about 3 to about 22 carbon atoms. Preferably, there are from about 3 to about 18 moles of ethylene oxide per mole of alcohol. The polyether can be conventionally end capped with acyl groups including methyl, benzyl, etc. groups. Examples of such ethoxylated alcohols include the condensation product of about 6 moles of ethylene oxide with 1 mole of tridecanol, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with coconut

fatty alcohol wherein the coconut alcohol is a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms and wherein the condensate contains about 6 moles of ethylene oxide per mole of alcohol, and
5 the condensation product of about 9 moles of ethylene oxide with the above-described coconut alcohol.

Examples of commercially available nonionic surfactants of this type include Tergitol 15-S-9 marketed by the Union Carbide Corporation. PLURAFAC[®] RA-40 marketed by
10 BASF Corp. Neodol 23-6.5 marketed by the Shell Chemical Company and Kyro EOB marketed by the Procter & Gamble Company.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene
15 oxide with propylene glycol can be used. The hydrophobic portion of these compounds has a molecular weight of from about 1,500 to 1,800 and of course exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion
20 tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product. Examples of compounds of this
25 type include certain of the commercially available Pluronic surfactants marketed by the Wyandotte Chemicals Corporation.

The condensation products of ethylene oxide with the product resulting from the reaction of propylene
30 oxide and ethylene diamine can be used. The hydrophobic base of these products consists of the reaction product of ethylene diamine and excess propylene oxide, said

base having a molecular weight of from about 2,500 to about 3,000. This base is condensed with ethylene oxide to the extent that the condensation product contains from about 40 to about 80 percent by weight of

5 polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic compounds marketed by the Wyandotte Chemical Corporation. Mixtures of the above surfactants

10 are also useful in the present invention.

Preferred nonionic surfactants used herein are the ethoxylated nonionics, both from the standpoint of availability and cleaning performance. Specific examples of alkoxylated nonionic surfactants include,

15 but are not limited to a benzyl ether of a C₆₋₂₄ linear alcohol 5-15 mole ethoxylate, PLURAFAC® RA-40, a straight chain alcohol ethoxylate, Triton CF-21 an alkyl aryl polyether, Triton CF-54, a modified polyethoxy adduct, and others.

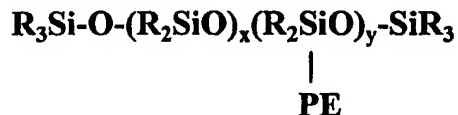
20 The second nonionic can comprise a silicon surfactant of the invention that comprises a modified dialkyl, preferably a dimethyl polysiloxane. The polysiloxane hydrophobic group is modified with one or more pendent hydrophilic polyalkylene oxide group or

25 groups. Such surfactants provide low surface tension, high wetting, antifoaming and excellent stain removal. We have found that the silicone nonionic surfactants of the invention, in a detergent composition with another nonionic surfactant can reduce the surface tension of

30 the aqueous solutions, made by dispensing the detergent with an aqueous spray, to between about 35 and 15 dynes/centimeter, preferably between 30 and 15

dynes/centimeter. The silicone surfactants of the invention comprise a polydialkyl siloxane, preferably a polydimethyl siloxane to which polyether, typically polyethylene oxide, groups have been grafted through a hydrosilation reaction. The process results in an alkyl pendent (AP type) copolymer, in which the polyalkylene oxide groups are attached along the siloxane backbone through a series of hydrolytically stable Si-C bond.

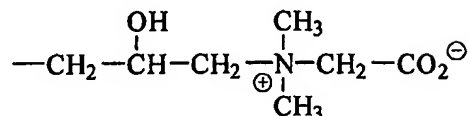
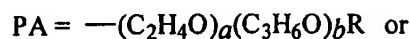
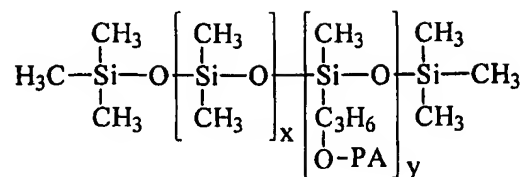
These nonionic substituted poly dialkyl siloxane products have the following generic formula:



15

wherein PE represents a nonionic group, preferably $-\text{CH}_2-(\text{CH}_2)_p-\text{O}-(\text{EO})_m(\text{PO})_n-\text{Z}$, EO representing ethylene oxide, PO representing propylene oxide, x is a number that ranges from about 0 to about 100, y is a number that ranges from about 1 to 100, m, n and p are numbers that range from about 0 to about 50, $m+n \geq 1$ and Z represents hydrogen or R wherein each R independently represents a lower (C_{1-6}) straight or branched alkyl.

Preferred silicone nonionic surfactants have the formula:



wherein x represent a number that ranges from about 0 to
 5 about 100, y represent a number that ranges from about 1
 to about 100, a and b represent numbers that
 independently range from about 0 to about 60, $a+b \geq 1$,
 and each R is independently H or a lower straight or
 branched (C_{1-6}) alkyl.

10 A second class of nonionic silicone surfactants is
 an alkoxy-end-blocked (AEB type) that are less preferred
 because the Si-O- bond offers limited resistance to
 hydrolysis under neutral or slightly alkaline
 conditions, but breaks down quickly in acidic
 15 environments.

Preferred surfactants are sold under the SILWET[®]
 trademark or under the ABIL[®] B trademark. One preferred
 surfactant, SILWET[®] L77, has the formula:



wherein $\text{R}^1 = -\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-[\text{CH}_2\text{CH}_2\text{O}]_z\text{CH}_3$; wherein z is 4 to
 16 preferably 4 to 12, most preferably 7-9.

To provide an alkaline pH, the composition
 25 comprises an alkalinity source. Generally, the

alkalinity source raises the pH of the composition to at least 10.0 in a 1 wt-% aqueous solutions and preferably to a range of from about 10.5 to 14. Such pH is sufficient for soil removal and sediment breakdown when the chemical is placed in use and further facilitates the rapid dispersion of soils. The general character of the alkalinity source is limited only to those chemical compositions which have a substantial aqueous solubility. Exemplary alkalinity sources include an alkali metal silicate, hydroxide, phosphate, or carbonate.

The alkalinity source can include an alkali metal hydroxide including sodium hydroxide, potassium hydroxide, lithium hydroxide, etc. Mixtures of these hydroxide species can also be used. Alkaline metal silicates can also act as a source of alkalinity for the detergents of the invention. Useful alkaline metal silicates correspond with the general formula ($M_2O:SiO_2$) wherein for each mole of M_2O there is less than one mole of SiO_2 . Preferably for each mole of SiO_2 there is from about 1 to about 100 moles of M_2O wherein M comprises sodium or potassium. Preferred sources of alkalinity are alkaline metal orthosilicate, alkaline metal metasilicate, and other well known detergent silicate materials.

The alkalinity source can include an alkali metal carbonate. Alkali metal carbonates which may be used in the invention include sodium carbonate, potassium carbonate, sodium or potassium bicarbonate or sesquicarbonate, among others. Preferred carbonates include sodium and potassium carbonates. These sources of alkalinity can be used the detergents of the

invention at concentrations about 5 wt-% to 70 wt-%, preferably from about 15 wt-% to 65 wt-%, and most preferably from about 30 wt-% to 55 wt-%.

In order to soften or treat water, prevent the
5 formation of precipitates or other salts, the composition of the present invention generally comprises components known as chelating agents, builders or sequestrants. Generally, sequestrants are those molecules capable of complexing or coordinating the
10 metal ions commonly found in service water and thereby preventing the metal ions from interfering with the functioning of deterative components within the composition. The number of covalent bonds capable of being formed by a sequestrant upon a single hardness ion
15 is reflected by labeling the sequestrant as bidentate (2), tridentate (3), tetradentate (4), etc. Any number of sequestrants may be used in accordance with the invention. Representative sequestrants include salts of amino carboxylic acids, phosphonic acid salts, water
20 soluble acrylic polymers, among others.

Suitable amino carboxylic acid chelating agents include N-hydroxyethyliminodiacetic acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl-ethylenediaminetriacetic
25 acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). When used, these amino carboxylic acids are generally present in concentrations ranging from about 1 wt-% to 50 wt-%, preferably from about 2 wt-% to 45 wt-%, and most preferably from about 3 wt-% to 40 wt-%.

30 Other suitable sequestrants include water soluble acrylic polymers used to condition the wash solutions under end use conditions. Such polymers include

polyacrylic acid, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed methacrylamide, hydrolyzed acrylamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, 5 hydrolyzed polymethacrylonitrile, hydrolyzed acrylonitrile methacrylonitrile copolymers, or mixtures thereof. Water soluble salts or partial salts of these polymers such as their respective alkali metal (for example, sodium or potassium) or ammonium salts can also 10 be used. The weight average molecular weight of the polymers is from about 4000 to about 12,000. Preferred polymers include polyacrylic acid, the partial sodium salts of polyacrylic acid or sodium polyacrylate having an average molecular weight within the range of 4000 to 15 8000. These acrylic polymers are generally useful in concentrations ranging from about 0.5 wt-% to 20 wt-%, preferably from about 1 to 10, and most preferably from about 1 to 5.

Also useful as sequestrants are alkali metal 20 phosphates, condensed and cyclic phosphates, phosphonic acids and phosphonic acid salts. Useful phosphates include alkali metal pyrophosphate, an alkali metal polyphosphate such a sodium tripolyphosphate (STPP) available in a variety of particle sizes. Such useful 25 phosphonic acids include, mono, di, tri and tetraphosphonic acids which can also contain groups capable of forming anions under alkaline conditions such as carboxy, hydroxy, thio and the like. Among these are phosphonic acids having the generic formula motif 30 $R_1N[CH_2PO_3H_2]_2$ or $R_2C(PO_3H_2)_2OH$, wherein R_1 may be $-(lower\ C_{1-6}alkylene)-N-[CH_2PO_3H_2]_2$ or a third $-(CH_2PO_3H_2)$ moiety; and wherein R_2 is selected from the group consisting of a

- lower (C_1 - C_6) alkyl. The phosphonic acid may also comprise a low molecular weight phosphonopolycarboxylic acid such as one having about 2-4 carboxylic acid moieties and about 1-3 phosphonic acid groups. Such
- 5 acids include 1-hydroxyethane-1,1-diphosphonic acid $CH_3C(OH)[PO(OH)_2]_2$; aminotri(methylenephosphonic acid) $N[CH_2PO(OH)_2]_3$; aminotri(methylenephosphonate), sodium salt
- 10 ONa
 $|$
 $POCH_2N[CH_2PO(ONa)_2]_2$;
 $|$
 OH
- 15 2-hydroxyethyliminobis(methylenephosphonic acid) $HOCH_2CH_2N[CH_2PO(OH)_2]_2$;
 diethylenetriaminepenta(methylenephosphonic acid) $(HO)_2POCH_2N[CH_2CH_2N[CH_2PO(OH)_2]_2]_2$;
 diethylenetriaminepenta(methylenephosphonate), sodium
- 20 salt $C_9H_{(28-x)}N_3Na_xO_{15}P_5$ ($x=7$);
 hexamethylenediamine(tetramethylenephosphonate),
 potassium salt $C_{10}H_{(28-x)}N_2K_xO_{12}P_4$ ($x=6$);
 bis(hexamethylene) triamine (pentamethylenephosphonic acid) $(HO)_2POCH_2N[(CH_2)_6N[CH_2PO(OH)_2]_2]_2$; and phosphorus
- 25 acid H_3PO_3 .
- The preferred phosphonate is aminotrimethylenephosphonic acid or salts thereof combined optionally with diethylenetriaminepenta(methylenephosphonic acid).
- When used as a sequestrant in the invention, phosphonic
- 30 acids or salts are present in a concentration ranging from about 0.25 to 25 wt%, preferably from about 1 to 20 wt%, and most preferably from about 1 to 18 wt% based on the solid detergent.

The invention may also comprise a solidifying agent to create a solid detergent mass from a blend of chemical components. Generally, any agent or combination of agents which provides a requisite degree of solidification and aqueous solubility may be used with the invention. A solidification agent may be selected from any organic or inorganic compound which imparts a solid character and/or controls the soluble character of the present composition when placed in an aqueous environment. The solidifying agent may provide for controlled dispensing by using solidification agents which have a relative increase in aqueous solubility. For systems which require less aqueous solubility or a slower rate of dissolution an organic nonionic or amide hardening agent may be appropriate. For a higher degree of aqueous solubility, an inorganic solidification agent or a more soluble organic agent such as urea.

Compositions which may be used with the present invention to vary hardness and solubility include amides such as stearic monoethanolamide, lauric diethanolamide, and stearic diethanolamide. Nonionic surfactants have also been found to impart varying degrees of hardness and solubility when combined with a coupler such as propylene glycol or polyethylene glycol. Nonionics useful in this invention include nonylphenol ethoxylates, linear alkyl alcohol ethoxylates, ethylene oxide/propylene oxide block copolymers such as the PluronicTM surfactants commercially available from BASF Wyandotte.

Nonionic surfactants particularly desirable as hardeners are those which are solid at room temperature

and have an inherently reduced aqueous solubility as a result of the combination with the coupling agent.

Other surfactants which may be used as solidifying agents include anionic surfactants which have high melting points to provide a solid at the temperature of application. Anionic surfactants which have been found most useful include linear alkyl benzene sulfonate surfactants, alcohol sulfates, alcohol ether sulfates, and alpha olefin sulfonates. Generally, linear alkyl benzene sulfonates are preferred for reasons of cost and efficiency.

Amphoteric or zwitterionic surfactants are also useful in providing detergency, emulsification, wetting and conditioning properties. Representative amphoteric surfactants include N-coco-3-aminopropionic acid and acid salts, N-tallow-3-iminodipropionate salts. As well as N-lauryl-3-iminodipropionate disodium salt, N-carboxymethyl-N-cocoalkyl-N-dimethylammonium hydroxide, N-carboxymethyl-N-dimethyl-N-(9-octadecenyl)ammonium hydroxide, (1-carboxyheptadecyl)trimethylammonium hydroxide, (1-carboxyundecyl)trimethylammonium hydroxide, N-cocoamidoethyl-N-hydroxyethylglycine sodium salt, N-hydroxyethyl-N-stearamidoglycine sodium salt, N-hydroxyethyl-N-lauramido- β -alanine sodium salt, N-cocoamido-N-hydroxyethyl- β -alanine sodium salt, as well as mixed alicyclic amines, and their ethoxylated and sulfated sodium salts, 2-alkyl-1-carboxymethyl-1-hydroxyethyl-2-imidazolinium hydroxide sodium salt or free acid wherein the alkyl group may be nonyl, undecyl, or heptadecyl. Also useful are 1,1-bis(carboxymethyl)-2-undecyl-2-imidazolinium hydroxide disodium salt and

oleic acid-ethylenediamine condensate, propoxylated and sulfated sodium salt. Amine oxide amphoteric surfactants are also useful. This list is by no means exclusive or limiting.

5 Other compositions which may be used as hardening agents with the composition of the invention include urea, also known as carbamide, and starches which have been made water soluble through an acid or alkaline treatment. Also useful are various inorganics which
10 either impart solidifying properties to the present composition and can be processed into pressed tablets for carrying the alkaline agent. Such inorganic agents include calcium carbonate, sodium sulfate, sodium bisulfate, alkali metal phosphates, anhydrous sodium
15 acetate and other known hydratable compounds. We have also found a novel hardening or binding agent for alkaline metal carbonate detergent compositions. We believe the binding agent comprises an amorphous complex of an organic phosphonate compound, sodium carbonate,
20 and water. The proportions of this binding hardening agent is disclosed in copending U.S. Serial No. _____ which is expressly incorporated by reference herein. This carbonate phosphate water binding agent can be used in conjunction with other hardening agents
25 such as a nonionic, etc.

The solidifying agents can be used in concentrations which promote solubility and the requisite structural integrity for the given application. Generally, the concentration of
30 solidifying agent ranges from about 5 wt-% to 35 wt, preferably from about 10 wt-% to 25 wt-%, and most preferably from about 15 wt-% to 20 wt-%.

The detergent composition of the invention may also comprise a bleaching source. Bleaches suitable for use in the detergent composition include any of the well known bleaching agents capable of removing stains from
5 such substrates as dishes, flatware, pots and pans, textiles, countertops, appliances, flooring, etc. without significantly damaging the substrate. These compounds are also capable of providing disinfecting and sanitizing antimicrobial efficacy in certain
10 applications. A nonlimiting list of bleaches include hypochlorites, chlorites, chlorinated phosphates, chloroisocyanates, chloroamines, etc.; and peroxide compounds such as hydrogen peroxide, perborates, percarbonates, etc.

15 Preferred bleaches include those bleaches which liberate an active halogen species such as Cl_2 , Br_2 , OCl^- , or OBr^- under conditions normally encountered in typical cleaning processes. Most preferably, the bleaching agent releases Cl_2 or OCl^- . A nonlimiting list
20 of useful chlorine releasing bleaches includes calcium hypochloride, lithium hypochloride, chlorinated trisodiumphosphate, sodium dichloroisocyanurate, chlorinated trisodium phosphate, sodium dichloroisocyanurate, potassium dichloroisocyanurate,
25 pentaisocyanurate, trichloromelamine, sulfondichloroamide, 1,3-dichloro 5,5-dimethyl hydantoin, N-chlorosuccinimide, N,N'-dichloroazodicarbonimide, N,N'-chloroacetylurea, N,N'-dichlorobiuret, trichlorocyanuric acid and hydrates thereof. Because of their higher
30 activity and higher bleaching efficacies the most preferred bleaching agents are the alkaline metal salts of dichloroisocyanurates and the hydrates thereof.

Generally, when present, the actual concentration of bleach source or agent (in wt-% active) may comprise about 0.5 to 20 wt-%, preferably about 1 to 10 wt-%, and most preferably from about 2 to 8 wt-% of the solid
5 detergent composition.

The composition of the invention may also comprise a defoaming surfactant useful in warewashing compositions. A defoamer is a chemical compound with a hydrophobe-hydrophile balance suitable for reducing the
10 stability of protein foam. The hydrophobicity can be provided by an oleophilic portion of the molecule. For example, an aromatic alkyl or alkyl group, an oxypropylene unit or oxypropylene chain, or other oxyalkylene functional groups other than oxyethylene
15 provide this hydrophobic character. The hydrophilicity can be provided by oxyethylene units, chains, blocks and/or ester groups. For example, organophosphate esters, salt type groups or salt forming groups all provide hydrophilicity within a defoaming agent.
20 Typically, defoamers are nonionic organic surface active polymers having hydrophobic groups, blocks or chains and hydrophilic ester groups, blocks, units or chains. However, anionic, cationic and amphoteric defoamers are also known. Phosphate esters are also suitable for use
25 as defoaming agents. For example, esters of the formula $RO-(PO_3M)_n-R$ wherein n is a number ranging from 1 to about 60, typically less than 10 for cyclic phosphates, M is an alkali metal and R is an organic group or M, with at least one R being an organic group such as an
30 oxyalkylene chain.

Suitable defoaming surfactants include ethylene oxide/propylene oxide blocked nonionic surfactants,

fluorocarbons and alkylated phosphate esters. When present defoaming agents may be present in a concentration ranging from about 0.1 wt-% to 10 wt-%, preferably from about 0.5 wt-% to 6 wt-% and most preferably from about 1 wt-% to 4 wt-% of the composition.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 is a drawing of a preferred embodiment of the packaged solid block detergent 10 of the invention. The detergent has a unique elliptical profile with a pinched waist. This profile ensures that this block with its particular profile can fit only spray on dispensers that have a correspondingly shaped pinch waisted elliptical profile location for the solid block detergent. We are unaware of any solid block detergent having this shape in the market place. The shape of the solid block ensures that no unsuitable substitute for this material can easily be placed into the dispenser for use in a warewashing machine. In Figure 1 the overall solid block product 10 is shown having a cast solid block 11 (revealed by the removal of packaging 12). The packaging includes a label 13 adhered to the packaging 12. The film wrapping can easily be removed using a weakened tear line 15 or fracture line or 15a incorporated in the wrapping.

The foregoing description of the invention provides an understanding of the individual components that can be used in formulating the solid block detergents of the invention. The following examples illustrate the preferred embodiments of the invention, the aqueous

surface tension and waxy soil cleaning properties of the invention and contain a best mode.

In the manufacture of the detergent, a dry bend powder can be made by blending powdered components into a complete formulation. Liquid ingredients can be pre-adsorbed onto dry components or encapsulated prior to mixing. Agglomerated materials can be made using known techniques and equipment. In manufacture of the solid detergent of the invention, the ingredients are mixed together at high shear to form a substantially homogenous consistency wherein the ingredients are distributed substantially evenly throughout the mass. The mixture is then discharged from the mixing system by casting into a mold or other container, by extruding the mixture, and the like. Preferably, the mixture is cast or extruded into a mold or other packaging system, that can optionally, but preferably, be used as a dispenser for the composition. The temperature of the mixture when discharged from the mixing system is maintained sufficiently low to enable the mixture to be cast or extruded directly into a packaging system without first cooling the mixture. Preferably, the mixture at the point of discharge is at about ambient temperature, about 30-50°C, preferably about 35-45°C. The composition is then allowed to harden to a solid form that may range from a low density, sponge-like, malleable, caulky consistency to a high density, fused solid, concrete-like block.

In a preferred method according to the invention, the mixing system is a twin-screw extruder which houses two adjacent parallel or counter rotating screws designed to co-rotate and intermesh, the extruder having

multiple ingredient inlets, barrel sections and a discharge port through which the mixture is extruded. The extruder may include, for example, one or more feed or conveying sections for receiving and moving the ingredients, a compression section, mixing sections with varying temperature, pressure and shear, a die section to shape the detergent solid, and the like. Suitable twin-screw extruders can be obtained commercially and include for example, Buhler Miag Model No. 62mm, Buhler Miag, Plymouth, Minnesota USA.

Extrusion conditions such as screw configuration, screw pitch, screw speed, temperature and pressure of the barrel sections, shear, throughput rate of the mixture, water content, die hole diameter, ingredient feed rate, and the like, may be varied as desired in a barrel section to achieve effective processing of ingredients to form a substantially homogeneous liquid or semi-solid mixture in which the ingredients are distributed evenly throughout. To facilitate processing of the mixture within the extruder, it is preferred that the viscosity of the mixture is maintained at about 1,000-1,000,000 cP, more preferably about 5,000-200,000 cP.

The extruder comprises a high shear screw configuration and screw conditions such as pitch, flight (forward or reverse) and speed effective to achieve high shear processing of the ingredients to a homogenous mixture. Preferably, the screw comprises a series of elements for conveying, mixing, kneading, compressing, discharging, and the like, arranged to mix the ingredients at high shear and convey the mixture through the extruder by the action of the screw within the

barrel section. The screw element may be a conveyor-type screw, a paddle design, a metering screw, and the like. A preferred screw speed is about 20-250 rpm, preferably about 40-150 rpm.

5 Optionally, heating and cooling devices may be mounted adjacent the extruder to apply or remove heat in order to obtain a desired temperature profile in the extruder. For example, an external source of heat may be applied to one or more barrel sections of the
10 extruder, such as the ingredient inlet section, the final outlet section, and the like, to increase fluidity of the mixture during processing through a section or from one section to another, or at the final barrel section through the discharge port. Preferably, the
15 temperature of the mixture during processing including at the discharge port, is maintained at or below the melting temperature of the ingredients, preferably at about 50-200°C.

 In the extruder, the action of the rotating screw
20 or screws will mix the ingredients and force the mixture through the sections of the extruder with considerable pressure. Pressure may be increased up to about 6,000 psig, preferably between about 5-150 psig, in one or more barrel sections to maintain the mixture at a
25 desired viscosity level or at the die to facilitate discharge of the mixture from the extruder.

 The flow rate of the mixture through the extruder will vary according to the type of machine used. In general, a flow rate is maintained to achieve a
30 residence time of the mixture within the extruder effective to provide substantially complete mixing of the ingredients to a homogenous mixture, and to maintain

the mixture at a fluid consistency effective for continuous mixing and eventual extrusion from the mixture without premature hardening.

When processing of the ingredients is complete, the mixture may be discharged from the extruder through the discharge port, preferably a shaping die for the product outside profile. The pressure may also be increased at the discharge port to facilitate extrusion of the mixture, to alter the appearance of the extrudate, for example, to expand it, to make it smoother or grainier in texture as desired, and the like.

The cast or extruded composition eventually hardens due, at least in part, to cooling and/or the chemical reaction of the ingredients. The solidification process may last from one minute to about 2-3 hours, depending, for example, on the size of the cast or extruded composition, the ingredients of the composition, the temperature of the composition, and other like factors. Preferably, the cast or extruded composition "sets up" or begins to harden to a solid form within about 1 minute to about 2 hours, preferably about 5 minutes to about 1 hour, preferably about 1 minute to about 20 minutes.

The above specification provides a basis for understanding the broad meets and bounds of the invention. The following examples and test data provide an understanding of the specific embodiments of the invention and contain a best mode. These examples are not meant to limit the scope of the invention that has been set forth in the foregoing description. Variation within the concepts of the invention are apparent to those skilled in the art.

Example IPROTOTYPE FOR TABLE 1

The following formula:

12.40 %	Water
2.5 %	A nonionic comprising a Benzyl capped, linear C ₁₀₋₁₄ alcohol 12.4 mole ethoxylate
0.5 %	ABIL [®] B 8852
1.572%	Defoamer
4.5 %	Spray-dried aminotrimethylene phosphonic acid, pentasodium salt
48.528%	Dense Ash (anhydrous Na ₂ CO ₃)
30 %	Sodium tripolyphosphate

5

was extruded from an extruder at a temperature of about 55°C forming a solid block detergent having a mass of about 3.0 kilograms. The extruder had 2 ingredient ports. In the first port, the dry ingredients including
10 the anhydrous sodium carbonate, the ABIL surfactant, sodium tripolyphosphate, the amino triethylene phosphonic acid sequestrants and 2/3 of the nonionic defoamer material were introduced. In port 2, the liquid ingredients including water, the nonionic, and
15 1/3 of the nonionic defoamer composition were added. The extruder blended the components into a uniform mass. After exiting the machine the blended mass hardened into a solid block detergent.

Example II

3.208 %	Water
2 %	A Benzyl capped, linear C ₁₀₋₁₄ alcohol 12.4 mole ethoxylate
2 %	PLURAFAC® RA-40
0.5 %	Silicone (SILWET® L-7602)
1.572%	Defoamer
4.390%	2-phosphono-butane 1,2,4-tricarboxylic acid
3.250%	NaOH, 50%
43.28 %	Sodium Carbonate (anhy.)
33.5 %	Sodium tripolyphosphate
6.3 %	hydroxy propylcellulose-coated (10%) chlorinated isocyanurate encapsulate

5 Example I was made as a cast solid. Example II and each of the detergents in Table 1 were prepared as a solid block as a prototype by combining the ingredients in the dishwasher without forming a solid. This method simulates the dispensing of a cast solid into the dish

10 machine. The formulation in Example I was used as a basis for the prototypes in Table 1. Example I was repeated as a Prototype I. Prototype II was made by increasing the concentration of the Table 1 listed surfactants. Prototype III was developed by

15 substituting the listed surfactants for the surfactants at the concentration listed in Prototype I, etc. Each test sample was prepared by adding a measured quantity of either the solid block or each individual ingredient

to a measured quantity of water in the test wash tank to model a cleaning solution derived from contacting a formulated detergent of the invention with water.

The soil removal properties of a blend of a first
5 nonionic surfactant and a second nonionic silicone
containing surfactant were measured using solid block
materials and prototype detergent solutions prepared as
shown in Examples I and II. The block detergents and
the prototype solutions were used in cleaning ware
10 containing lipstick soil. The test was conducted using
the following protocol.

Test Procedures

15 A 10-cycle spot, film, protein, and lipstick
removal test was used to compare formulas 1 and 2 and
other similar formulae under different test conditions.
In this test procedure, clean, clean-lipstick stained
and milk-coated, Libbey glasses were washed in an
20 institutional dish machine (a Hobart C-44) together with
a lab soil and the test detergent formula. Milk coating
were created by dipping clean glasses in whole milk and
conditioning the glasses for an hour at 100°F and 65% RH.
The concentrations of each detergent were maintained
25 constant throughout the 10-cycle test.

The lab soil used is a 50/50 combination of beef
stew and hot point soil. The hot point soil is a
greasy, hydrophobic soil made of 4 parts Blue Bonnet all
vegetable margarine and 1 part Carnation Instant Non-Fat
30 milk powder.

In the test, the milk-coated, stained glasses are used to test the soil removal ability of the detergent formula, while the initially clean glasses are used to test the anti-redeposition ability of the detergent formula. At the end of the test, the glasses are rated for spots, film, protein, and lipstick removal. The rating scale is from 1 to 5 with 1 being the best and 5 being the worst results.

The data produced by this experiment is displayed below in Table 1. In the table, surfactants in the detergent formula at particular use concentrations and soil load were tested for surface tension at room temperature and 160°F and lipstick removal protocols using a one cycle and a two to ten cycle test sequence.

TABLE I
Correlation of Surface Tension Results to 10-Cycle Warewash Test Results

Prototype Based on Example I	Surfactants used in Detergent Formula from Example II	Detergent Conc., ppm	Total Surfactant Conc., ppm	Soil Load, ppm	Surface Tension at RT, dyne/cm	Surface Tension at 160°F, dyne/cm	Lipstick** Cycle 2-10	Lipstick** Cycle I
I	2.5% LF-428	800	24	2000	33.14	26.11	1	1
	0.5% Abil B 8852	1000	30	2000	32.60	25.69	1	1
	2.5% LF-428							
II	0.5% Abil B 8852	800	36	2000	30.81	30.76*	5	5
	2% LF-428							
	2% RA-40							
III	0.5% SILWET* L-7602							
	2% LF-428	800	36	2000	30.76	29.95	1	1
	2% RA-40							
IV	0.5% Abil B 8852	800	36	2000	31.70	30.26	1	1
	2% LF-428							
	2% RA-40							
V	0.5% Abil B 8847	800	17.5	2000	<20	<20	1	1
	0.875% FC-170-C							
	1.313% SILWET* L-77							
VI	0.5% Tegopren 5840	800	24	2000	30.6	26.5	1	1
	2.5% Tegin L-90							
	2% LF-428	800	41.6	2000	31.8	28.5	2	1
VII	2% RA-40							
	1.2% MT-70							
	1.2% MT-70	800	9.6	2000	27.0	24.0	1	2
VIII	2% LF-428	800	41.6	2000	31.0	29.2	1	2.5
	2% RA-40							
	0.6% MT-70							
IX	0.6% JAQ Quat							

TABLE 1 (Continued)

Prototype Based on Example I	Surfactants in Detergent Formula	Detergent Conc., ppm	Total Surfactant Conc., ppm	Soil Load, ppm	Surface Tension at R.T. dynes/cm	Surface Tension at 100°F. dynes/cm	Lipstick** Cycle 2-10	Lipstick** Cycle 1
X	2% LF-428 2% RA-40 0.5% SILWET* L-7210	800	36	2000	31.36	30.98*	1.3	1
XI	0.5% Tegopren 5840	800	4	2000	34.5	28.7	2.5	1
XII	0.5% Tegopren 5840 2.5% Triton CF-21	800	24	2000	29.8	26.3	1.3	1.5
XIII	0.5% Tegopren 5840 2.5% Triton CF-54	800	24	2000	31.2	27.1	2.25	1
XIV	2% LF-428 2% RA-40 0.5% Abil B 8878	800	36	2000	32.27	30.81*	1.5	4
XV	3.5% LF-428	1000	35	2000	32.85	32.73	3.75	3.75
XVI	2% LF-428 2% RA-40 0.583% LP-300	800	36.7	2000	32.0	30.37	3	3
XVII	1.75% LF-428 1.75% RA-40	1000	35	2000	31.61	34	5	5
XVIII	2% LF-428 2% RA-40 0.5% Abil B 8873	800	36	2000	30.22	29.73*	4	5

* The Wilhelmy plate became hydrophobicized after the surface tension measurements. Some data are deemed unreliable.

** A grading of 1 means no lipstick remains, a grading of 5 means 100% remains.

Descriptions of the Surfactants Used and Their
Manufacturers

LF-428: Benzyl ether of a C₁₀₋₁₄ linear alcohol 12.4 mole
5 ethoxylate (Ecolab); Plurafac RA-40: Modified
ethoxylated straight chain alcohol (BASF Corp.);
Surfadone LP-300: N-dodecyl pyrrolidone (International
Specialty Products); Monawet MT-70: Di-tridecyl sodium
sulfosuccinate, 70% (Mona Industries Inc.); JAQ Quat:
10 N-alkyl (3% C₁₂, 95% C₁₄, 2% C₁₆) dimethyl benzyl
ammonium chloride dihydrate (Huntington); Abil B 8852,
8847, 8878, 8873; Tegopren 5840: Polysiloxane polyether
copolymers (Goldschmidt Chemical Corporation); Silwet L-
7602, L-7210, L-77: Polyalkylene oxide-modified
15 dimethylpolysiloxanes (Union Carbide Corporation);
Triton CF-21: Alkylaryl polyether (Union Carbide
Corporation); Triton CF-54: Modified polyethoxy adduct
(Union Carbide Corporation); Fluorad FC-170-C:
Fluorinated alkyl polyoxyethylene ethanols (3M Company)
20 Tegin L-90: Glyceryl monolaurate (Goldschmidt Chemical
Corporation)

Table 1 indicates a rough correlation between a low
surface tension and improved waxy soil cleaning
properties. We have found that when the surfactant
25 blend achieves a surface tension that measures less than
about 30 dynes/cm at 160°F, and that the surfactant
blend in an alkaline detergent block can remove lipstick
soil with other soils without redeposition in a single
cycle.

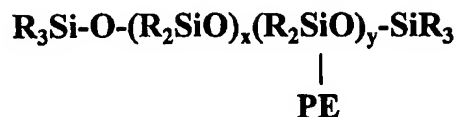
30 The foregoing specification, examples and data
provide a sound basis for understanding the technical
advantages of the invention. However, since the
invention can comprise a variety of embodiments, the
invention resides in the claims hereinafter appended.

WE CLAIM:

1. An alkaline detergent composition comprising:
 - (a) an effective soil removing amount of a source
5 of alkalinity; and
 - (b) an effective soil removing amount of a nonionic surfactant blend comprising:
 - (i) a nonionic surfactant comprising a
hydrophobic group and an $-(EO)_x$ group, wherein
10 x is a number of about 1 to 100; and
 - (ii) a nonionic silicone surfactant comprising
a hydrophobic silicone group and a pendent
hydrophilic polyalkylene oxide group;wherein the detergent exhibits enhanced waxy-fatty soil
15 removing capacity.
2. The detergent of claim 1 wherein the detergent
comprises a solid block having a mass of at least 100
grams.
20
3. The detergent of claim 2 wherein the detergent is
packaged within a flexible wrapping.
4. The detergent of claim 1 comprising a powder.
25
5. The detergent of claim 1 comprising a pellet.

6. The detergent of claim 1 wherein the silicone surfactant has the formula:

5



10 wherein PE represents $-\text{CH}_2-(\text{CH}_2)_p-\text{O}-(\text{EO})_m(\text{PO})_n-\text{Z}$, x is a number that ranges from about 0 to about 100, y is a number that ranges from about 1 to 100, p is 0 to 6, m and n are numbers that range from about 0 to about 50, $m+n \geq 1$, and Z represents hydrogen or R and each R
15 independently represents a lower (C_{1-6}) alkyl.

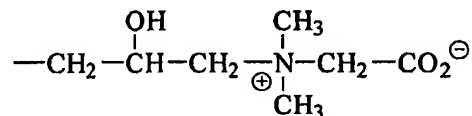
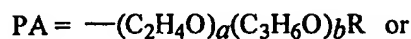
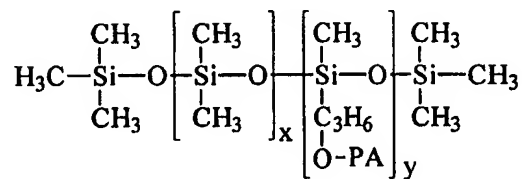
7. The detergent of claim 1 wherein the source of alkalinity comprises an alkali metal hydroxide.

20 8. The detergent of claim 1 wherein the source of alkalinity comprises an alkali metal carbonate.

9. The detergent of claim 1 wherein the detergent additionally comprises a hardness sequestering agent.

10. The detergent of claim 1 wherein the silicone surfactant has the formula:

5



wherein x represent a number that ranges from about 0 to
 10 about 100, y represent a number that ranges from about 1
 to about 100, a and b represent numbers that
 independently represent numbers that range from about 0
 to about 60,
 a+b ≥ 1 and R is hydrogen or a lower (C₁₋₆) alkyl.

15

11. The detergent of claim 1 wherein the nonionic surfactant comprises a linear alcohol ethoxylate or an alkylphenolethoxylate.

20 12. The detergent of claim 1 wherein the nonionic surfactant comprises a benzyl capped C₈₋₁₂ linear alcohol 6 to 16 mole ethoxylate.

13. The detergent of claim 9 wherein the sequestrant
 25 comprises an amino trialkylene phosphonic acid sodium salt.

14. The detergent of claim 9 wherein the sequestrant additionally comprises a 2-phosphono-butane-1,2,4-tricarboxylic acid sodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) or mixtures thereof.

15. The detergent of claim 9 wherein the sequestrant comprises sodium tripolyphosphate and amino trimethylene phosphonic acid sodium salt, 2-phosphono-butane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) or mixtures thereof.

16. The detergent composition of claim 2, wherein the detergent comprises

- (a) about 5 to 60 wt% of Na_2CO_3 ; and
- (b) about 1 to 50 wt% of a hardness sequestering agent selected from the group consisting of sodium tripolyphosphate, an organic phosphonate sequestrant, and mixtures thereof;

wherein the solid block detergent has a mass of at least 0.5 kilograms.

17. The detergent of claim 16 wherein the phosphonate sequestrant comprises an amino trimethylene phosphonic acid sodium salt.

18. The detergent of claim 17 wherein the sequestrant additionally comprises a 2-phosphono-butane-1,2,4-tricarboxylic acid sodium salt, 1-hydroxyethylidene-1,1-

diphosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) or mixtures thereof..

19. The detergent of claim 16 wherein the detergent is
5 packaged in a flexible polyolefin film.

20. A solid block detergent composition, the detergent comprising:

(a) an effective soil removing amount of a source
10 of alkalinity;

(b) an effective amount of a hardness sequestering agent; and

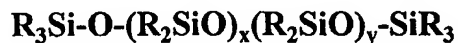
(c) an effective soil removing amount of nonionic surfactant composition comprising:

15 (i) a nonionic surfactant comprising a hydrophobic group and an $-(EO)_x$ group, wherein x is a number of about 1 to 60 group; and

(ii) a silicone surfactant comprising a hydrophobic silicone group and a pendent
20 hydrophilic polyalkylene oxide group;

wherein the block has a mass of at least 100 grams and is packaged within a flexible wrapping and the detergent exhibits enhanced waxy-fatty soil cleaning capacity.

25 21. The detergent of claim 20 wherein the silicone surfactant has the formula:



|
PE

30

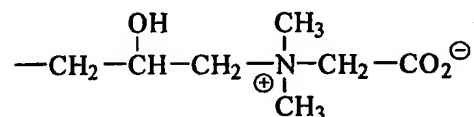
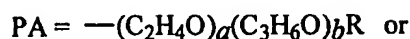
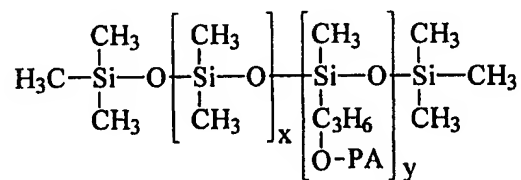
wherein PE represents $-CH_2-(CH_2)_p-O-(EO)_m(PO)_n-Z$, x is a number that ranges from about 0 to about 100, y is a

number that ranges from about 1 to 100, $x+y \geq 1$, p is 0 to 6, m and n are numbers that range from about 0 to about 50, $m+n \geq 1$, and Z represents hydrogen or R and each R represents a lower (C_{1-6}) alkyl.

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22. The detergent of claim 20 wherein the silicone surfactant has the formula:

10



wherein x represent a number that ranges from about 0 to about 100, y represent a number that ranges from about 1 to about 100, $x+y \geq 1$, a and b represent numbers that independently represent numbers that range from about 0 to about 60, $a+b \geq 1$ and R is hydrogen or a lower (C_{1-6}) alkyl.

20

23. The detergent of claim 20 wherein the nonionic surfactant comprises a linear alcohol ethoxylate or an alkylphenol-ethoxylate.

24. The detergent of claim 20 wherein the nonionic surfactant comprises a benzyl capped C₈₋₁₂ linear alcohol 6 to 16 mole ethoxylate.
- 5 25. The detergent of claim 20 wherein the sequestrant comprises an amino trialkylene phosphonic acid sodium salt.
26. The detergent of claim 25 wherein the sequestrant
10 additionally comprises a 2-phosphono-butane-1,2,4-tricarboxylic acid sodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) or mixtures thereof.
- 15 27. The detergent of claim 20 wherein the sequestrant comprises an amino trialkylene phosphonic acid sodium salt or a 2-phosphono-butane-1,2,4-tricarboxylic acid sodium salt 1-hydroxyethylidene-1,1-diphosphonic acid, diethylenetriamine-penta(methylenephosphonic acid) or
20 mixtures thereof.
28. The detergent of claim 20 wherein the sequestrant comprises sodium tripolyphosphate and amino trimethylene phosphonic acid sodium salt, 2-phosphono-butane-1,2,4-
25 tricarboxylic acid or mixtures thereof.
29. The detergent composition of claim 20, wherein the detergent comprises:
- (a) about 5 to 60 wt% of Na₂CO₃; and
- 30 (b) about 3 to 40 wt% of a hardness sequestering agent selected from the group consisting of sodium

tripolyphosphate, an organic phosphonate
sequestrant, and mixtures thereof;

wherein the solid block detergent has a mass of at least
0.5 kilograms.

5

30. The detergent of claim 20 wherein the detergent is
packaged in a flexible polyolefin film.

31. The detergent of claim 1 wherein the nonionic
10 surfactant comprises a benzyl capped C₈₋₁₂ linear alcohol
6 to 16 mole ethoxylate.

32. The detergent of claim 1 additionally comprising a
source of chlorine.

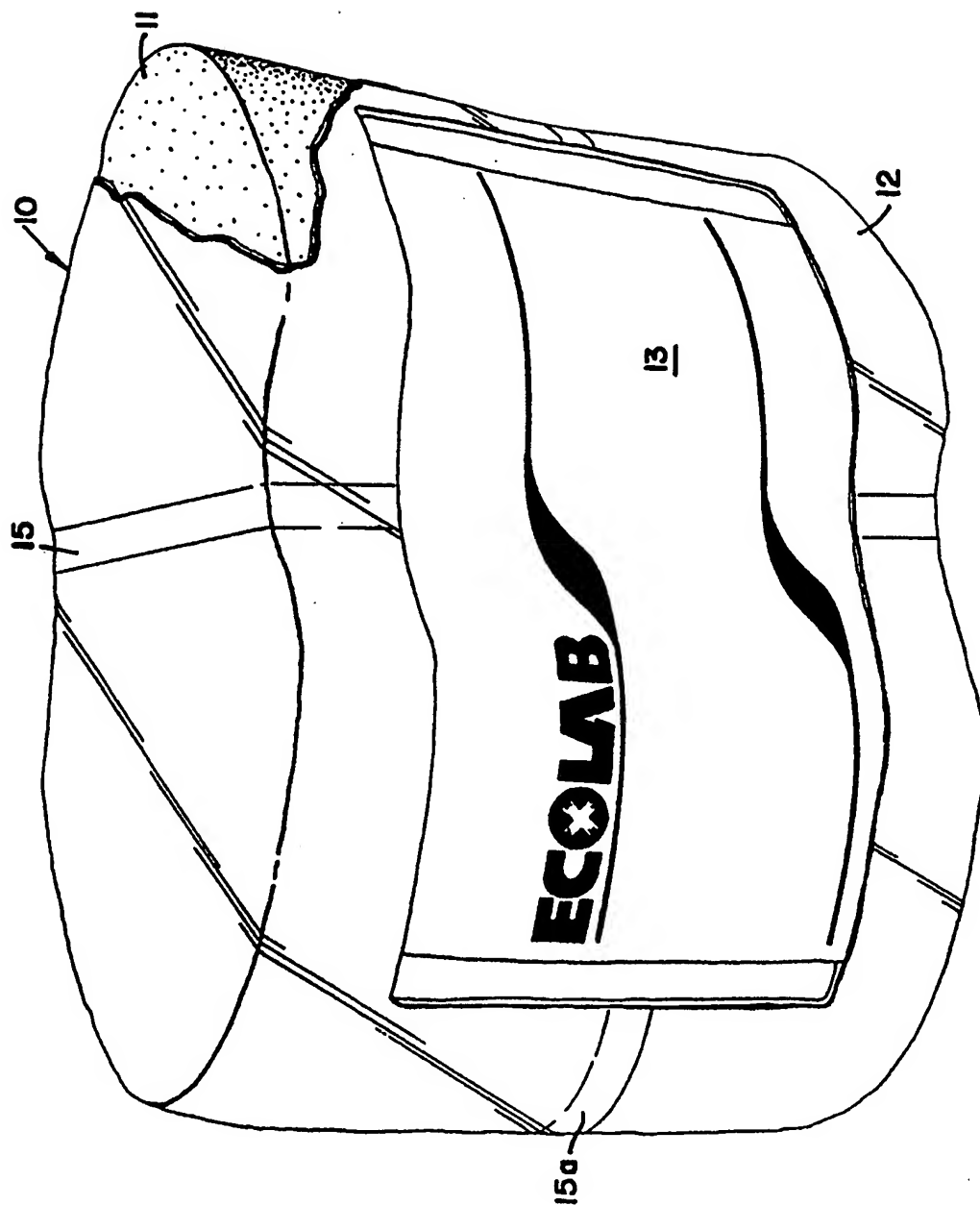
15

33. The detergent of claim 32 wherein the source of
chlorine comprises an encapsulated chlorine source.

34. The detergent of claim 20 additionally comprising a
20 chlorine source.

35. The detergent of claim 34 wherein the chlorine
source comprises an encapsulated chlorine source.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/00452

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/825 C11D3/37 C11D17/00 C11D3/06 C11D3/02
C11D3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 136 045 A (GAULT TERRELL W ET AL) 23 January 1979 see column 8, lines 5-57; column 16, lines 52-55; examples I, V-VIII ---	1, 4-6, 9-11
X	GB 2 245 908 A (COLGATE PALMOLIVE CO) 15 January 1992 see page 8, line 27 - page 10, line 16; examples 1, 4 ---	1, 4-6, 9-11
X	US 5 474 698 A (ROLANDO JOHN J ET AL) 12 December 1995 see column 3, line 12 - column 8, line 47; column 11, line 64 - column 12, line 39; example 1 --- -/--	1, 2, 6, 9-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 May 1998

Date of mailing of the international search report

12/06/1998

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/00452

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 08553 A (ECOLAB INC) 21 March 1996 see page 5, line 10 - page 14, line 13; page 17, line 13 - page 19, line 13; page 20, line 36 - page 2, line 10; example II ---	1-35
A	WO 95 18212 A (ECOLAB INC) 6 July 1995 see page 3, line 18 - page 7, line 6; page 9, line 32 - page 16, line 11 -----	1-35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 98/00452

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4136045 A	23-01-1979	CA 1085697 A	16-09-1980
GB 2245908 A	15-01-1992	US 4818421 A	04-04-1989
		AT 229188 A	15-05-1994
		AU 2229588 A	13-04-1989
		BE 1002291 A	20-11-1990
		CH 678535 A	30-09-1991
		DE 3832017 A	27-04-1989
		DK 514588 A	18-03-1989
		FR 2637609 A	13-04-1990
		GB 2210070 A, B	01-06-1989
		GR 1000493 B	30-07-1992
		NL 8802301 A	17-04-1989
		SE 8803236 A	22-03-1989
US 5474698 A	12-12-1995	AU 671938 B	12-09-1996
		AU 1258995 A	17-07-1995
		CA 2169757 A	06-07-1995
		CN 1128544 A	07-08-1996
		EP 0753047 A	15-01-1997
		JP 9507259 T	22-07-1997
		NZ 277385 A	24-02-1997
		WO 9518211 A	06-07-1995
WO 9608553 A	21-03-1996	US 5603776 A	18-02-1997
		AU 2437895 A	29-03-1996
		CA 2198004 A	21-03-1996
		EP 0781322 A	02-07-1997
WO 9518212 A	06-07-1995	AU 682244 B	25-09-1997
		AU 1514095 A	17-07-1995
		BR 9407721 A	04-03-1997
		CA 2170501 A	06-07-1995
		CN 1139452 A	01-01-1997
		EP 0740698 A	06-11-1996
		JP 9507260 T	22-07-1997
		NZ 278722 A	24-03-1997
		US 5674831 A	07-10-1997
		US 5698513 A	16-12-1997
		ZA 9410376 A	01-07-1996

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No. _____

PCT/US 98/00452

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9518212 A		ZA 9410379 A	01-07-1996

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